Experimental study on zirconium carbide ceramics expected to be used as coatings for fuel of fourth-generation nuclear reactors

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Introduction

By 2020-2040 a fourth generation nuclear power plant should be built. This new generation of reactors should lead to a fuel material burning and improved radioactive waste reprocessing or partial recycling. It should also ensure an excellent safety level while remaining financially viable and meet broader needs (such as hydrogen production or sea-water desalination). Zirconium carbide ceramics are one of the foreseen materials for fuel cladding of fourth-generation gas-cooled nuclear reactors (GFR[1] and VHTR[2]). It must act as a diffusion barrier for the volatile fission products generated inside the fuel such as xenon, iodine and cesium. This study particularly focused on how stoichiometry influences carbide oxidation. Zirconium carbide is a refractory ceramic but it easily oxidizes under heat, so it is necessary to monitor material oxidation and its influence on the stoichiometry, thanks to RBS[3] analysis.

Experimental methods

Seven sets of zirconium carbide samples were synthesized thanks to a sintering method, with $ZrC_{0.95}O_{0.05}$ and $ZrC_{0.80}O_{0.20}$ stoichiometries and densities ranging from 88% to 99% as summarized in table 1.

Table 1: Seven sets of zirconium carbide samples: stoichiometries and densities.

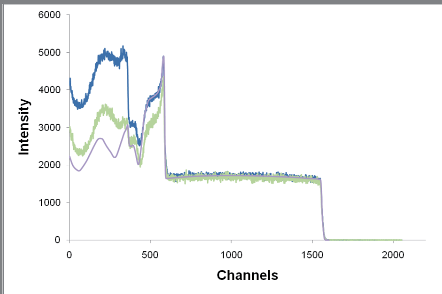
Stoichiometries	Densities
$ZrC_{0.80}O_{0.20}$	97 %
$ZrC_{0.80}O_{0.20}$	98 %
$ZrC_{0.80}O_{0.20}$	98.5 %
$ZrC_{0.95}O_{0.05}$	88 %
$ZrC_{0.95}O_{0.05}$	89 %
$ZrC_{0.95}O_{0.05}$	96 %
$ZrC_{0.95}O_{0.05}$	99 %

Each of these samples was first polished to micron. They have then been annealed after-polishing in a furnace under about 1.10^{-7} bar vacuum at 1000 ° C for 10 hours. This annealing allowed the defects related to surface polishing to be cured. Each sample was then examined by RBS analysis under a double charged ion beam at 7.5 MeV. From the experimental spectra, it was possible to determine the final stoichiometry of the sample and the thickness of the oxidized layer using the simulation software named SimNra.

Results and discussion

Figure 1 shows the $ZrC_{0,8}O_{0,2}$ sample with a density of 98%, a grain size of 1.58 µm, a sintering time of 3 hours and 30 minutes. The samples showed a susceptibility to oxidation during annealing despite a correct and controlled vacuum. Indeed, the oxygen peak was higher for the annealed sample than for the blank sample. Controlling oxidation during annealing of implanted xenon samples was therefore essential. Thus, working under a controlled argon-hydrogen atmosphere (so as to maintain a reducing atmosphere) was preferred in case of high temperature annealing in order to limit oxidation.

Figure 1 : RBS Spectra of ZrC0,8O0,2 98 % : comparison between an annealing and a blank samples. Purple curve, the simulated spectrum by SimNra ; blue curve, the spectrum for an after-polishing sample at 1000 ° C for 10h and green curve for the blank sample.



Conclusion

The RBS analysis showed a slight oxidation of the sample surface but the sample core did not change in depth. Despite this sensitivity to oxidation, zirconium carbide is a ceramic to consider as coatings for fuel of fourth generation reactors.

[1] Gas-cooled Fast Reactor
[2] Very High Temperature Reactor
[3] Rutherford Backskattering Spectroscopy

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